and NMR spectrum), and 116 mg of 7 as a pale yellow, viscous oil: NMR ($CDCl_3$) δ 1.25 (m, 2 H), 1.68 (bs, 3 H), 1.82 (d, J = 0.9 Hz, 3 H), 2.17 (m, 2 H), and 7.04 and 7.11 (s's, 5 H each); mass spectrum M.+ 280.1257, (calcd for $C_{19}H_{20}S$, 280.1254).

Conversion of 7 to *cis*-2-Phenylcyclopropanecarboxylic Acid (8). A solution of 80 mg of 7 in 2 ml of 1:1 dichloromethane–pyridine was cooled in a dry ice–acetone bath and was treated with a slight excess of ozone.[14] The reaction mixture was allowed to warm to 25 °C, poured into 25 ml of ether, and washed several times with 1 N hydrochloric acid. The extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure, giving a yellow, viscous oil (ir 1702 cm^{-1}).

The residue was dissolved in 10 ml of 10% sodium hydroxide in 50% aqueous ethanol. The mixture was refluxed for 40 min, cooled, poured into 20 ml of water, and extracted with ether. The aqueous layer was acidified with hydrochloric acid and was extracted with two 10-ml portions of ether. The ether extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure, leaving 15 mg of a tan solid whose NMR spectrum was identical with that of *cis*-2-phenylcyclopropanecarboxylic acid (8).[15] No peaks representing *trans*-2-phenylcyclopropanecarboxylic acid were present.

Reaction of 6 with Thiophenol. To a solution of 200 mg of 6 in 0.5 ml of hexadeuteriobenzene in an NMR tube was added 120 mg of thiophenol. The reaction mixture was thoroughly mixed and the rate of reaction was monitored with time by NMR. The reaction displayed an induction period of ~2 min, being essentially complete in 15 min at 39 °C. The resulting mixture was poured into 10 ml of ether and was extracted twice with 5-ml portions of 1 M sodium hydroxide, washed with water and saturated sodium chloride, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was distilled in a microstill at 115 °C (0.07 mm), giving a pale yellow, viscous oil: NMR of 9 ($CDCl_3$) δ 0.88 (dd, J = 5.0 and 8.1 Hz), 1.08 (dd, J = 2.3 and 8.1 Hz), 1.47 (s), 1.63 (dd, J = 2.3 and 5.0 Hz), 1.84 and 1.88 (broadened s's), 7.18; **10**, δ 1.33 (s), 1.87 and 2.08 (broadened s's), 71.8 (the AMX double doublets are obscured by the more intense resonances of 9); mass spectrum M.+ 294.1426 (calcd for $C_{20}H_{22}S$, 294.1442).

Reaction of 3 with Thiophenol. A solution of 430 mg (2.86 mmol) of 3 in 5 ml of benzene was added to 314 mg (2.86 mmol) of thiophenol dissolved in 5 ml of benzene. The reaction mixture was allowed to stand at room temperature for 3 h, at which time analysis by NMR indicated complete reaction. The benzene solution was washed with 15 ml of 10% sodium hydroxide and water, and was dried ($MgSO_4$). The benzene was removed under reduced pressure giving 656 mg of a pale yellow oil (11): bp ~50 °C (0.05 mm) in a molecular still; NMR ($CDCl_3$) δ 0.90 (s, 6 H), 0.98 (s, 6 H), 1.13 (m, 1 H), 1.83 (d, J = 1.6 Hz, 3 H), 1.92 (d, J = 2.2 Hz, 3 H), and 7.07 (m, 5 H); mass spectrum M.+ 260.1597 (calcd for $C_{17}H_{14}S$, 260.1608).

Ozonolysis of 11. A solution of 76 mg (0.30 mmol) of 11 in 1.75 ml of dichloromethane and 0.25 ml of pyridine[14] was cooled in a dry ice–acetone bath and ozone was bubbled through the solution for 15 s. The reaction mixture was allowed to warm to 25 °C and was analyzed directly by GLC on a Carbowax 20M column showing the presence of acetone by comparison of retention time with authentic material and admixture.

Registry No.—2, 4544-23-4; 3, 13303,30-5; 6, 40922-91-6; 7, 58873-30-6; 8, 939-89-9; 9, 58873-31-7; 11, 58873-32-8; thiophenol, 108-98-5.

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Trichloromethyl Chloroformate. Reaction with Amines, Amino Acids, and Amino Alcohols

Keisuke Kurita,* Toru Matsumura, and Yoshio Iwakura

Department of Industrial Chemistry, College of Technology, Seikei University, Kichijoji, Musashino-shi, Tokyo, Japan

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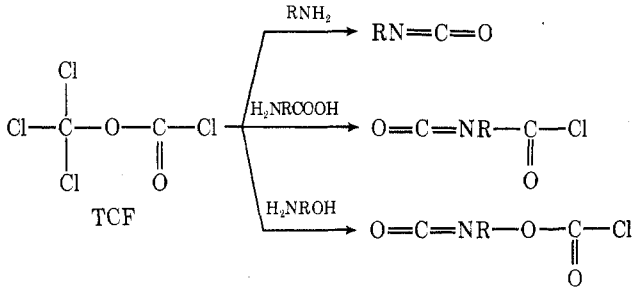
The title compound, trichloromethyl chloroformate (TCF), is of interest in that it is a potential substitute for phosgene, which presents a severe hazard in laboratory use because of its volatility and high toxicity. Although TCF is also toxic,[1] it is a dense liquid (bp 128 °C, d_{15}^{15} 1.65) with vapor pressure of only 10 mm at 20 °C. Thus TCF is more easily handled with safety, and seems to have significant advantages over phosgene.

Hentschel studied the decomposition of TCF and reactions with some organic compounds and found that phenyl isocyanate was formed by the action of TCF on 1,3-diphenylurea.[2] The reaction with alcohols to give carbonates has also been reported.[3] TCF was recently reported to be used as a substitute for phosgene in the preparation of *N*-carboxy-α-amino acid anhydrides; 1 mol of TCF provided the equivalent of 2 mol of phosgene in the NCA synthesis.[4]

To extend our knowledge of the reactivity of TCF, it was of interest to compare other reactions of TCF with those of phosgene. This paper describes the reaction of TCF with amines, amino acids, and amino alcohols to give the corresponding isocyanates, isocyanato acid chlorides, and isocyanato chloroformates.



The reactions of TCF with aniline were carried out under conditions similar to those employed in the phosgene method. As expected, phenyl isocyanate was obtained in high yields (78–89%) either from the hydrochloride or the free base. It was also confirmed that 0.5 mol of TCF was sufficient to convert 1 mol of the amine to the isocyanate.

Treatment of *p*-phenylenediamine hydrochloride with TCF in dioxane, on the other hand, gave only poor yields (23% or less) of the diisocyanate, even though the reaction was carried out under almost the same conditions used with phosgene. When the free base was used instead of the hydrochloride, the yield of the diisocyanate was improved to 47%. An attempted reaction of hexamethylenediamine hydrochloride with TCF in dioxane was unsuccessful and the hydrochloride was recovered. This result is presumably due to the high basicity of hexamethylenediamine compared to that of aromatic amines,

the more stable hydrochloride derived from the amine of higher basicity being less reactive to electrophilic attack.

The reactions of amino acids or amino alcohols with phosgene are interesting since they provide in one step molecules with two different functional groups, namely isocyanato acid chlorides or isocyanato chloroformates. The synthesis of 6-isocyanatohexanoyl chloride by the action of phosgene on the amino acid was reported to be attained only by using an additional reagent such as hydrogen chloride, thionyl chloride, or phosphorus pentachloride besides phosgene.[5] When TCF was used in this preparation, however, 6-isocyanatohexanoyl chloride was obtained in 73% yield without an additional reagent. TCF also reacted smoothly with 3-aminopropanoic acid, and in contrast to phosgene, 3-isocyanatopropanoyl chloride was obtained quantitatively (97%).

In contrast to the preparation of alkyl isocyanato acid chlorides, the TCF method with aromatic amino acids gave results similar to those with phosgene.[5] Treatment of *o*-aminobenzoic acid with TCF resulted in the formation of isatoic anhydride in a quantitative yield, as observed with phosgene. The reaction between *m*-aminobenzoic acid and TCF failed to give the corresponding isocyanato acid chloride, and only an unidentified white solid was obtained. It was confirmed that an additional reagent such as phosphorus pentachloride was necessary to prepare *o*-isocyanatobenzoyl chloride (85% yield) as in the phosgene method.[5]

Reactions of amino alcohols with TCF proceeded similarly to those with phosgene.[6] 3-Aminopropanol and 2-aminoethanol gave 3-isocyanatopropyl chloroformate and 2-isocyanatoethyl chloroformate, respectively, in 53 and 21% yields.

Thus it was found that TCF is far superior to phosgene in the alkyl isocyanato acid chlorides syntheses, but was comparable to phosgene in the preparations of phenyl isocyanate, aromatic isocyanato acid chlorides, and alkyl isocyanato chloroformates.

Experimental Section[7]

Phenyl Isocyanate. To a mixture of 12.95 g (0.1 mol) of aniline hydrochloride and 100 ml of dry dioxane was added 6.3 ml (10.4 g, 0.05 mol) of TCF. The mixture was heated at 60 °C; after 1.5 h of stirring, it became a clear solution. Heating was discontinued after 3.5 h and the solvent was removed under reduced pressure. The residue was distilled at 70–73.5 °C (36 mm) to give 10.6 g (89%) of phenyl isocyanate. It was redistilled almost quantitatively, bp 75–77 °C (39 mm) [lit.[8] 55–57 °C (16 mm)].

***p*-Phenylene Diisocyanate. A. From the Hydrochloride.** To 100 ml of dry dioxane were added 14.48 g (0.08 mol) of *p*-phenylenediamine hydrochloride and 51 ml (84.2 g, 0.4 mol) of TCF. The mixture was heated at reflux for 20 h. The unreacted hydrochloride was filtered off and the filtrate was evaporated under reduced pressure. The residual white, crystalline solid was sublimed under vacuum to give 3.0 g (23%) of *p*-phenylene diisocyanate. It was sublimed again at 85 °C (7 mm) to give colorless crystals, mp 92–94 °C (lit.[8] 94–96 °C).

B. From the Free Base. To a solution of 8.64 g (0.08 mol) of *p*-phenylenediamine in 100 ml of dry dioxane was added 20.5 ml (34.8 g, 0.16 mol) of TCF with stirring. Precipitation took place instantaneously. After refluxing the mixture for 20 h, the undissolved white solid was filtered off and the filtrate was evaporated. The residual solid gave 6.0 g (47%) of *p*-phenylene diisocyanate on sublimation.

3-Isocyanatopropanoyl Chloride. To 250 ml of dry dioxane were added 12.6 g (0.1 mol) of powdered 3-aminopropanoic acid hydrochloride and then 37.9 ml (62.6 g, 0.3 mol) of TCF with stirring. The mixture became a clear solution after heating at 55 °C for 4.5 h. The heating was continued for an additional 6.5 h and then the solvent was removed under reduced pressure. The residual oil was distilled to give 13.0 g (97%) of 3-isocyanatopropanoyl chloride, bp 77–80 °C (10 mm) [lit.[5] 91–91.5 °C (24.5 mm)].

6-Isocyanatohexanoyl chloride was synthesized by virtually the same procedure, bp 112–113 °C (5 mm) [lit.[5] 114 °C (6 mm)].

Reaction of *o*-Aminobenzoic Acid with TCF. A. Without PCl_5. A mixture of 10.0 g (0.073 mol) of *o*-aminobenzoic acid and 36.8 ml (60.7 g, 0.3 mol) of TCF in 150 ml of dry dioxane was refluxed for 6 h. The resulting clear solution was evaporated to give a white solid. It was recrystallized from tetrahydrofuran to give 10.0 g (92%) of isatoic anhydride, mp 241–243 °C dec (lit.[5] 242–243 °C dec).

B. With PCl_5. To a mixture of 10.0 g of *o*-aminobenzoic acid and 36.8 ml of TCF in 150 ml of dry dioxane was added 15.2 g (0.073 mol) of phosphorus pentachloride with stirring. Phosphorus pentachloride went into solution in 1 h. The solution was allowed to stand at room temperature overnight and then the solvent was removed under reduced pressure. The residue was distilled two times to give 11.2 g (85%) of *o*-isocyanatobenzoyl chloride, bp 108–109.5 °C (2 mm), mp 30–32 °C (lit.[5] 32 °C).

3-Isocyanatopropyl Chloroformate. To a solution of 48.4 ml (79.8 g, 0.4 mol) of TCF in 250 ml of dry dioxane was added 7.5 g (0.1 mol) of 3-aminopropanol dropwise over a period of 1 h with cooling in an ice bath. The mixture was stirred with cooling for 30 min and then left standing at room temperature overnight. The solution was evaporated under reduced pressure and the residue was distilled to give 10.2 g of distillate boiling at 65–105 °C (7 mm). Fractional redistillation afforded 0.5 g of a forerun boiling at 23–60 °C (1 mm) and 8.7 g (53%) of 3-isocyanatopropyl chloroformate boiling at 70–74.5 °C (1 mm) [lit.[6] 82 °C (1.5 mm)]. The forerun was considered to consist of mostly 3-chloropropyl isocyanate from its boiling range [lit.[6] 34 °C (1.5 mm)] and ir spectrum.

2-Isocyanatoethyl Chloroformate. 2-Aminoethanol (6.1 g, 0.1 mol) was treated with 24.2 ml (40 g, 0.2 mol) of TCF in 250 ml of dry dioxane at 55–60 °C for 6 h. Fractional distillation gave 0.7 g (3%) of 2-chloroethyl isocyanate boiling at 41.5–45 °C (13 mm) [lit.[6] 35–36 °C (13 mm)], 3.2 g (21%) of 2-isocyanatoethyl chloroformate boiling at 89.5–90 °C (14 mm) [lit.[6] 86–87 °C (13 mm)], and 1 g (6%) of 2-oxazolidone boiling at 160–165 °C (2 mm), mp 86–88 °C (lit.[6] 89 °C).

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Registry No.—Phenyl isocyanate, 103-71-9; aniline hydrochloride, 142-04-1; *p*-phenylene diisocyanate, 104-49-4; *p*-phenylenediamine hydrochloride, 624-18-0; *p*-phenylenediamine, 106-50-3; 3-isocyanatopropanoyl chloride, 3729-19-9; 3-aminopropanoic acid hydrochloride, 6057-90-5; 6-isocyanatohexanoyl chloride, 3729-18-8; *o*-aminobenzoic acid, 118-92-3; isatoic anhydride, 118-48-9; *o*-isocyanatobenzoyl chloride, 5100-23-2; 3-aminopropanol, 156-87-6; 3-isocyanatopropyl chloroformate, 13107-90-9; 3-chloropropyl isocyanate, 13010-19-0; 2-aminoethanol, 141-43-5; 2-chloroethyl isocyanate, 1943-83-5; 2-isocyanatoethyl chloroformate, 13107-89-6; 2-oxazolidone, 497-25-6; TCF, 23213-83-4; PCl_5, 10026-13-8.

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An Electron Spin Resonance Study of the Radical Anion of 7,8-Dimethylene-1,3,5-cyclooctatriene

Ronald L. Blankespoor* and Colleen M. Snavely

Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109

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Several examples of pericyclic reactions in radical anions are known where the stereochemistry is the same as that of the excited state of the neutral molecule.[1] If these reactions are concerted, the parallel mode of reaction of the radical anions with the excited states is predicted by the highest occupied molecular orbital (HOMO) method.[2] Bauld and Cessac[3] have recently noted that the butadiene–cyclobutene